ALKYD RESINS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

Mixtures of free fatty acids in natural oil and alkyd resin samples have been analyzed using a μBondapak Free Fatty Acid column in conjunction with a ternary mobile phase. Variation of the mobile phase composition allows "fingerprinting" as well as quantitation of the fatty acid components. Samples can be analyzed in ten minutes by this method. The results of the application of this technique to the identification of oil sources of fatty acids as well as the production of fatty acids during alkyd resin synthesis are given. Good agreement is observed for fatty acid compositions determined via HPLC with those obtained by gas chromatographic methyl ester analysis.

INTRODUCTION

The development of chromatographic methods for the analysis of fatty acids has reached a high level of sophistication over the last two decades. Reviews by Dallas, et. al. (1) and Metcalfe (2) attest to the magnitude of research effort in this area. The emphasis placed upon the analysis of these materials derives

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in part from their importance as items of commerce in the fields of protective coatings, foods, and pharmaceutical products (3).

The most widely applied technique for fatty acid analysis is gas chromatography (GC) (4,5). Application of this technique usually requires the formation of volatile derivatives (i.e. methyl esters) to affect separation. These derivatization procedures are extremely well developed (6), but do require the attendant time and expense associated with their use. In addition, there have been reports in the literature of incomplete conversion of the fatty acids to their methyl ester derivative (7) as well as chemical transformation of the acid prior to chromatographic analysis (8).

High performance liquid chromatography (HPLC) of fatty acids has been developed in recent years as an alternative to the conventional GC approach. Limited success was experienced with this technique prior to 1975 as noted in the reviews of Cooper and Anders (9) and Aitzetmüller (10). The last five years have seen the development of a number of novel separation schemes based upon the use of bonded phase support materials. These methods have frequently involved the separation of the methyl esters (11-16), or the formation of derivatives having chromaphoric (17-27) or fluorescence (28,29) properties. Impressive separations have also been recorded using a variety of gradient elution methods (23-27,30,31) and argentation chromatography has been effective in segregating unsaturated fatty acids from the aliphatic acids (11,30,32-34).

Unfortunately, many of the above methods require the formation of fatty acid derivatives and are prohibitively long. For example, several gradient separations require an analysis time of 150 (27) and 250 (23) minutes, respectively. These factors mitigate against employing some of the above chromatographic assays in an industrial environment, where rapidly obtained results are important in identifying oil types, changes in fatty acid composition, and to monitor reaction kinetics and products.

In 1976, Bidlingmeyer, et. al. (35) reported on the development of a μBondapak Free Fatty Acid column. This column/isocratic mobile phase combination allowed the rapid separation of many of the fatty acids contained in important commercial oils. Since the introduction of this reverse phase column, there have been a limited number of papers describing its use in margarine analysis (36), in the isolation of minor fatty acids in tall oil (37), and a vague report of its use in the coatings industry (38).

In this publication, we will show how the above described column, with appropriate variation of the mobile phase, can be used for the identification and quantitation of fatty acid mixtures derived from industrial oil and alkyd resin samples. Examples will be given which show how unique chromatographic "fingerprints" are obtained for each oil and how these can be used to make semi-quantitative conclusions regarding changes in oil fatty acid composition during alkyd resin synthesis.

EXPERIMENTAL

Apparatus. Chromatographic data were obtained using a Waters Associates (Milford, Mass.) Model ALC 202 liquid chromatograph equipped with a Waters Model 6000 dual reciprocating piston pump and Model U6K injector. Detection of the solutes was facilitated by using a Waters Model R401 differential refractometer. Chromatograms were recorded on a Sargent Model SR recorder. Attenuation settings for the refractometer were typically 4 to 16X yielding suitable responses on the recorder set at a 12.5 mV full-scale range.

A Waters μBondapak Fatty Acid Analysis Column (4 mm i.d. x 30 cm length) was utilized to fractionate the fatty acid mixtures. The mobile phase consisted of a ternary mixture of tetrahydrofuran (THF), acetonitrile (CH_3CN), and water, the sum of these three solvents being equal to 105 volume units (39). The level of tetrahydrofuran was kept constant at 25 volume units to prevent precipitation of the fatty acids. Retention of the solutes was adjusted by varying the ratio of acetonitrile to water. Addition of two volume units of acetic acid was found to be very beneficial in improving peak symmetry.

Reagents. Mobile phase solvents were obtained from the following sources: acetonitrile (ACS Certified Grade) and tetrahydrofuran (Certified Grade) from Fisher Scientific (Pittsburgh, Pa.) and glacial acetic acid (Reagent Grade) from J. T. Baker Co. (Phillipsburg, NJ). All solvents including distilled water were used without further purification.

Fatty acid standards were obtained from Applied Science Laboratories, Inc. (State College, Pa.), Analabs, Inc. (North Haven, Conn.) and Supelco, Inc. (Bellefonte, Pa.). Commercial samples of fatty acids, oils, and alkyd resins were obtained from Ashland Chemical Co. (Columbus, Ohio), Emery Industries, Inc. (Cincinnati, Ohio), Lilly Industrial Coatings (Indianapolis, Ind.), and Armak Co. (Chicago, Ill.). The saturated fatty acid standards (100 mg) were dissolved in 1.0 ml of tetrahydrofuran, while unsaturated fatty acid standards (25 mg) were dissolved in 0.5 ml of the same solvent. Commercial samples were diluted one to ten by volume in tetrahydrofuran.

Procedure. Samples were injected using a 25.0 μL Precision Sampling Corp. (Baton Rouge, La.), Series B-110, Pressure-Lok liquid syringe. Typical injection volumes were in the range of 0.5-5.0 μL. Eluent flow rates were measured using a Kimax 10.0 ml burette and a Huer stopwatch (1.0×10^{-2} sec. resolution).

Laboratory saponification of the oils and alkyd resins was accomplished using a modification of the procedures of Ast (40) and Metcalfe, Schmitz, and Pelka (41). Two milliliters of vegetable oil were refluxed with 50 ml of saturated KOH/methanol in a 100 ml round bottom flask equipped with a N_2 sparge for 10 minutes. The sample was then removed and placed in an ice bath for two minutes. Twenty milliliters of distilled water were added to the flask and the pH adjusted to 2 with dilute hydrochloric acid. After the sample was sufficiently cool, 15-25 ml of n-hexane was added to extract the fatty acids. Agitation was then applied to transfer the solutes to the n-hexane followed by separation of the two layers in a separatory funnel. The n-hexane was then removed using gentle heating and vacuum aspiration. Finally, the concentrated acids were redissolved in tetrahydrofuran.

A similar procedure was used to prepare the fatty acids from alkyd resins. In this case, a quantity of 4-5 ml of the resin was used initially. An additional extraction step using ethyl ether was performed after the refluxing stage to remove the unsaponifiable matter. With practice, the above saponification scheme yielded a sample ready for injection in 30 minutes.

RESULTS AND DISCUSSION

Tables I and II summarize the retention behavior of model solutes on the Free Fatty Acid column for the two most frequently used mobile phase compositions in this study. The observed trends in retention volume are identical to those previously reported (35). The retention of fatty acids increases with carbon number for both the saturated and unsaturated acids. As the degree of unsaturation increases, for acids having the same carbon number, their retention volumes decrease correspondingly. This is amply illustrated by the decrease in retention volume in going from stearic acid to linolenic acid.

The substitution of two double bonds into a given fatty acid structure reduces its retention volume by an increment approximately equivalent to that observed in reducing its carbon number by a factor of two. Hence, there is peak overlap between certain saturated and unsaturated moieties, i.e. myristoleic and lauric acid. Such a situation can be partially alleviated by changing the mobile phase composition for the fatty acid mixture being chromatographed.

TABLE I

RETENTION VOLUMES OF SATURATED FATTY ACIDS

Solute	Retention Volumes (ml)[a]	
Caproic Acid (n-hexanoic)	3.8[b]	4.0[c]
Caprylic Acid (n-octanoic)	4.1	4.4
Capric Acid (n-decenoic)	4.5	5.1
Lauric Acid (n-dodecenoic)	5.2	5.9
Myristic Acid (n-tetradecenoic)	6.1	7.1
Palmitic Acid (n-hexadecenoic)	7.2	8.8
Stearic Acid (n-octadecenoic)	9.1	11.2
Arachidic Acid (n-eicosanoic)	11.0	14.3
Behenic Acid (n-docosanoic)	14.0	18.2

[a]Measured from point of injection

[b]Mobile phase composition: 43/37/25 parts by volume acetonitrile/water/tetrahydrofuran

[c]Mobile phase composition: 43/37/25/2 parts by volume acetonitrile/water/tetrahydrofuran/glacial acetic acid

The regularity in these retention trends is of great aid in identifying the individual fatty acids in the oil. Coupled with compositional data from GC results (42,43), oil types can readily be identified. We have used these data along with infrared and nuclear magnetic resonance techniques, to identify unknown solutes.

The addition of acetic acid to the mobile phase not only improves peak symmetry but increases the retention volume of the solutes. The result is usually improved resolution between the chromatographic peaks in the fatty acid mixture. For some cis/

TABLE II

RETENTION VOLUMES OF UNSATURATED FATTY ACIDS

Solute	Retention Volumes (ml)[a]	
Myristoleic Acid (cis-9-tetradecenoic)	5.2[b]	6.2[c]
Palmitoleic Acid (cis-9-hexadecenoic)	5.9	7.5
Palmitelaidic Acid (trans-9-hexadecenoic)	6.0	7.6
Oleic Acid (cis-9-octadecenoic)	7.2	9.1
Elaidic Acid (trans-9-octadecenoic)	6.3	9.4
Linoleic Acid (cis-cis-9,12-octadecadienoic)	6.5	8.1
Linolelaidic Acid (trans,trans-9,12-octadecadienoic)	6.4	8.5
Linolenic Acid (cis,cis,cis-9,12,15-octadecatrienoic)	6.2	7.3
Cis-5-Eicosenoic Acid	7.3	12.2
Erucic Acid (cis-13-docosenoic)	8.1	14.1
Nervonic Acid (cis-15-tetracosenoic)	9.6	18.2

[a]Measured from point of injection

[b]Mobile phase composition: 43/37/25 parts by volume acetonitrile/water/tetrahydrofuran

[c]Mobile phase composition: 43/37/25/2 parts by volume acetonitrile/water/tetrahydrofuran/glacial acetic acid

trans isomer pairs, there is a reversal in elution order observed by the addition of acetic acid.

The factors responsible for the retention volume differences observed for the two mobile phase compositions are difficult to elucidate. Both solvent compositions have similar solubility parameters (15.4 and 15.8 Hildebrands) (44). Undoubtedly, reten-

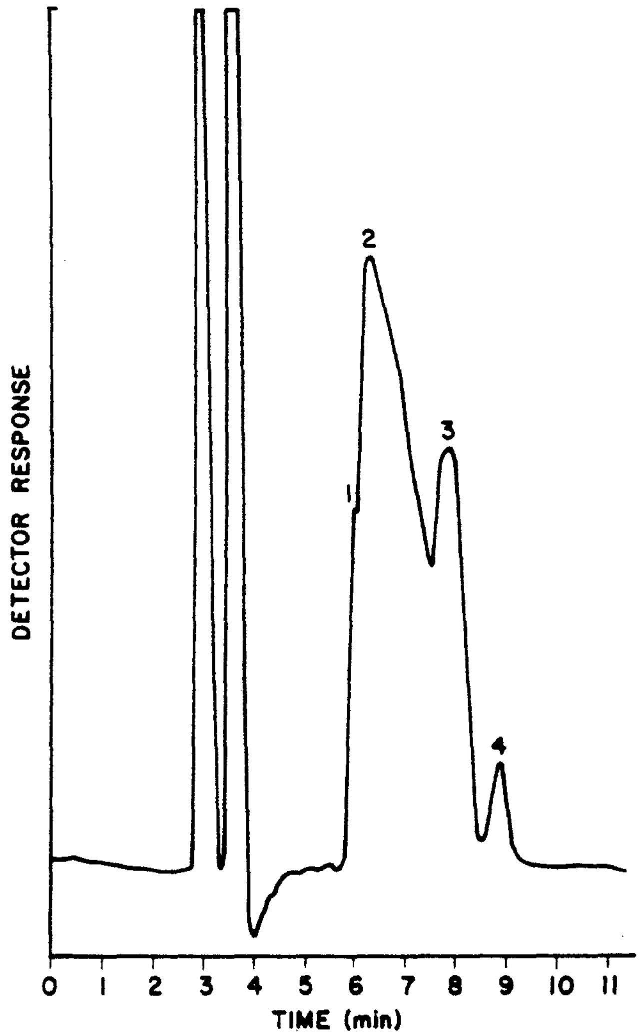

Figure 1: Chromatogram of commercially saponified soybean oil fatty acids. Identification of acids: (1) linolenic; (2) linoleic and palmitic; (3) oleic; (4) stearic. Mobile phase composition: 40/40/25, water/acetonitrile/tetrahydrofuran by volume.

tion is governed in part by hydrophobicity of the solutes (45,46) and the relative donor, dipole, and acceptor profiles (47) of the solvents making up the mobile phase.

An excellent example of the effect of the mobile phase composition is in the separation of a soybean fatty acid mixture as shown in Figures 1-3. Figure 1 is a rather poorly defined chromatogram showing incomplete resolution of linolenic, linoleic, palmitic, and oleic acids. Clearly, not even semi-quantitative

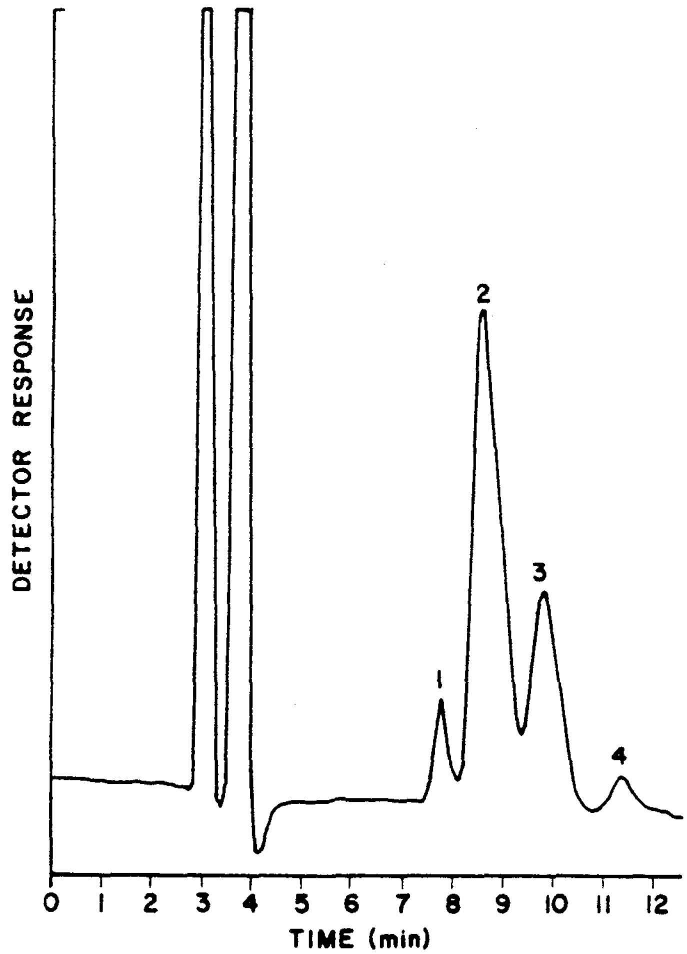

Figure 2: Chromatogram of commercially saponified soybean oil fatty acids. Identification of acids: (1) linolenic; (2) palmitic and linoleic; (3) oleic; (4) stearic. Mobile phase composition: 37/43/25, water/acetonitrile/ tetrahydrofuran by volume.

information can be obtained from this chromatogram developed with a 40/40/25 mixture of $H_2O/CH_3CN/THF$. By adjusting the water to acetonitrile ratio slightly, a dramatic improvement in peak resolution is obtained as illustrated in Figure 2. Here there is sufficient separation of the major fatty acid peaks in the soybean oil to allow conclusions to be drawn as to alteration in composition. Further improvement is realized by the addition of 2 parts by volume of acetic acid. This sharpens the peaks sufficiently so as to allow the analyst to see the palmitic acid as a

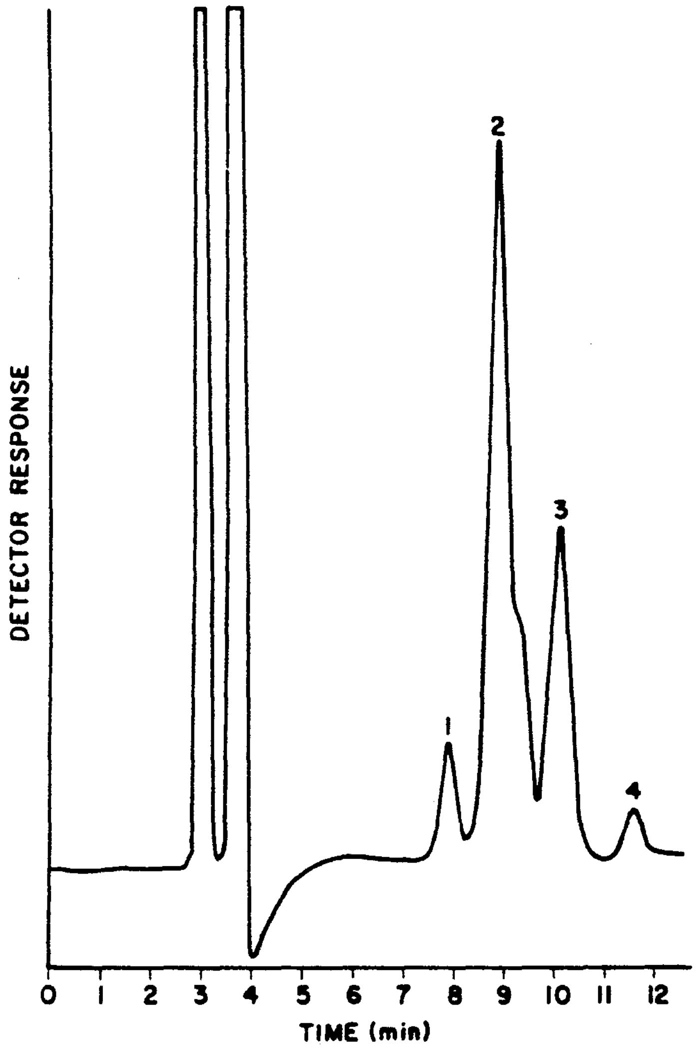

Figure 3: Chromatogram of commercially saponified soybean oil fatty acids. Identification of acids: (1) linolenic; (2) palmitic and linoleic; (3) oleic; (4) stearic. Mobile phase composition: 37/43/25/2, water/acetonitrile/tetrahydrofuran/acetic acid by volume.

shoulder on the linoleic acid peak in Figure 3. Similar improvements can be achieved with other oil mixtures by adjusting the ratio of solvents in the mobile phase (48). In general, we have achieved the most successful separations using the acidified solvent mixture.

Oil Results. Figures 4-6 are typical chromatographic profiles for commercially saponified oils. These were developed using a

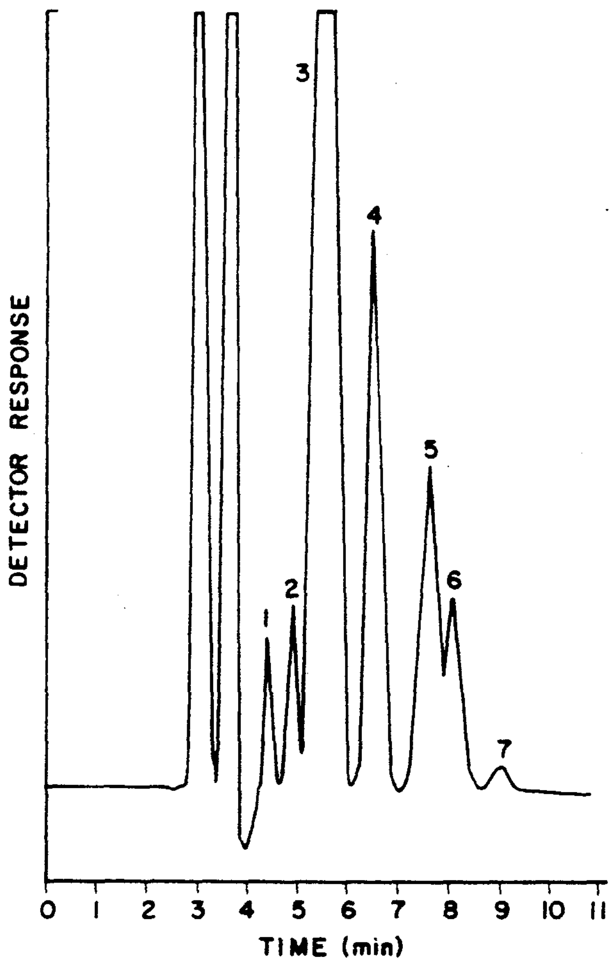

Figure 4: Chromatogram of commercially saponified coconut oil fatty acids. Identification of acids: (1) caprylic; (2) capric; (3) lauric; (4) myristic; (5) palmitic and linoleic; (6) oleic; (7) stearic. Mobile phase composition: 40/40/25, water/acetonitrile/tetrahydrofuran by volume.

ternary mobile phase of 40/40/25 parts by volume of acetonitrile/water/tetrahydrofuran. The peaks appearing at retention volumes less than 4.0 ml are due to the solvent vacancy effect (49). Their presence eliminates the possibility of calculating accurate capacity factors (K') for the fatty acids (50). It is readily apparent by intercomparing Figures 4-6 that one can identify the source (oil) of the fatty acid mixture. This can be accomplished within a 10 minute elution time frame.

Figure 4 represents a commercially saponified coconut oil

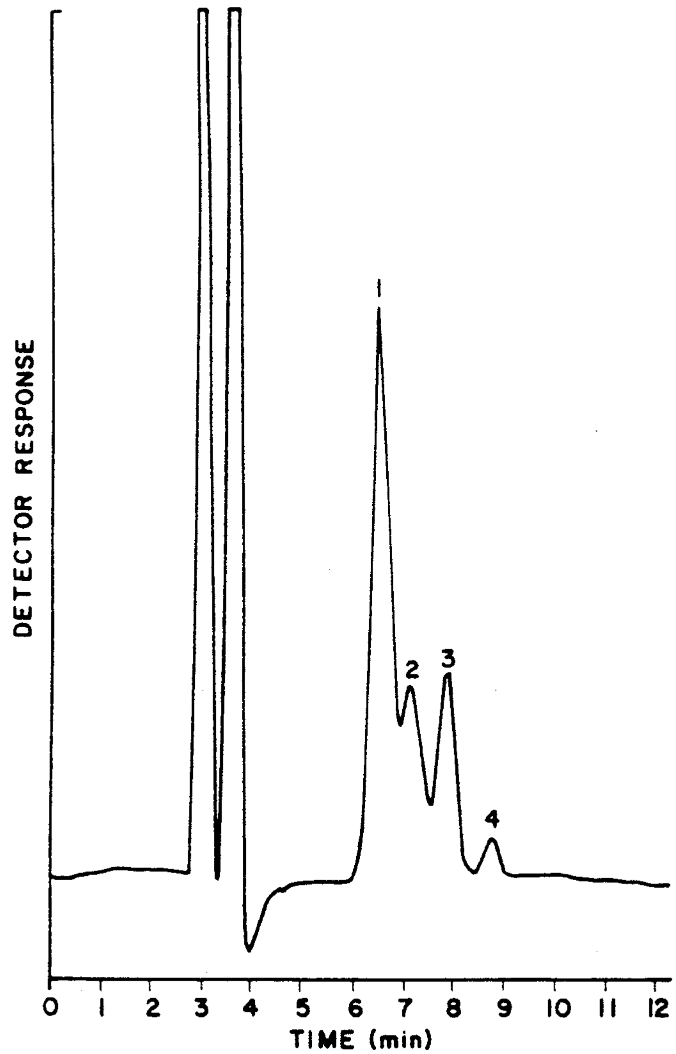

Figure 5: Chromatogram of commercially saponified linseed oil fatty acids. Identification of acids: (1) linolenic; (2) palmitic and linoleic; (3) oleic; (4) stearic. Mobile phase composition same as in Figure 4.

fatty acid mixture. All of the major fatty acids comprising this saponified oil are present in the chromatogram, with the exception of linoleic acid which elutes under the palmitic acid, peak number 5. The elution order of the components in the chromatogram is in agreement with trends previously discussed. The fused peak pair, palmitic and linoleic acids, were confirmed by the method of standard addition with highly purified fatty acid standards. This type of procedure was used in addition to the previously discussed methods to identify any ambiguities in the peak elution order.

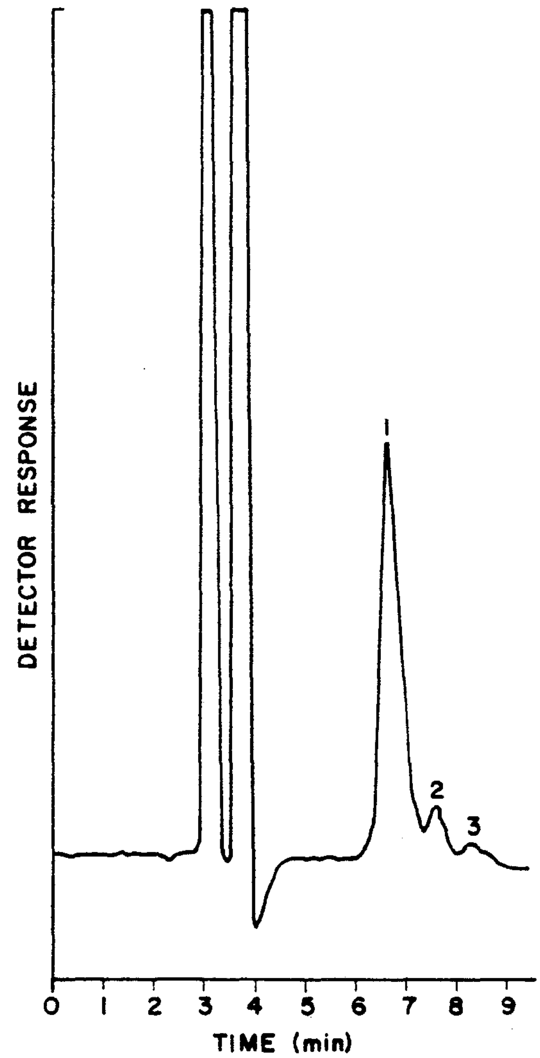

Figure 6: Chromatogram of commercially saponified tung oil fatty acids. Identification of acids: (1) eleostearic, linoleic, linolenic, and palmitic; (2) oleic; (3) stearic. Mobile phase composition same as in Figure 5.

Figure 5 illustrates the elution pattern for linseed oil, whose major fatty acid components are unsaturated C_{18} fatty acids. In this chromatogram, linolenic, the fatty acid having the most unsaturation, elutes first followed by linoleic, oleic, and the saturated analogue, stearic acid. The fifth component, palmitic acid, present to the extent of approximately 6% by weight, is eluted along with the linoleic acid (16% by weight) (42). The chromatogram in Figure 6 represents tung oil fatty acids. The

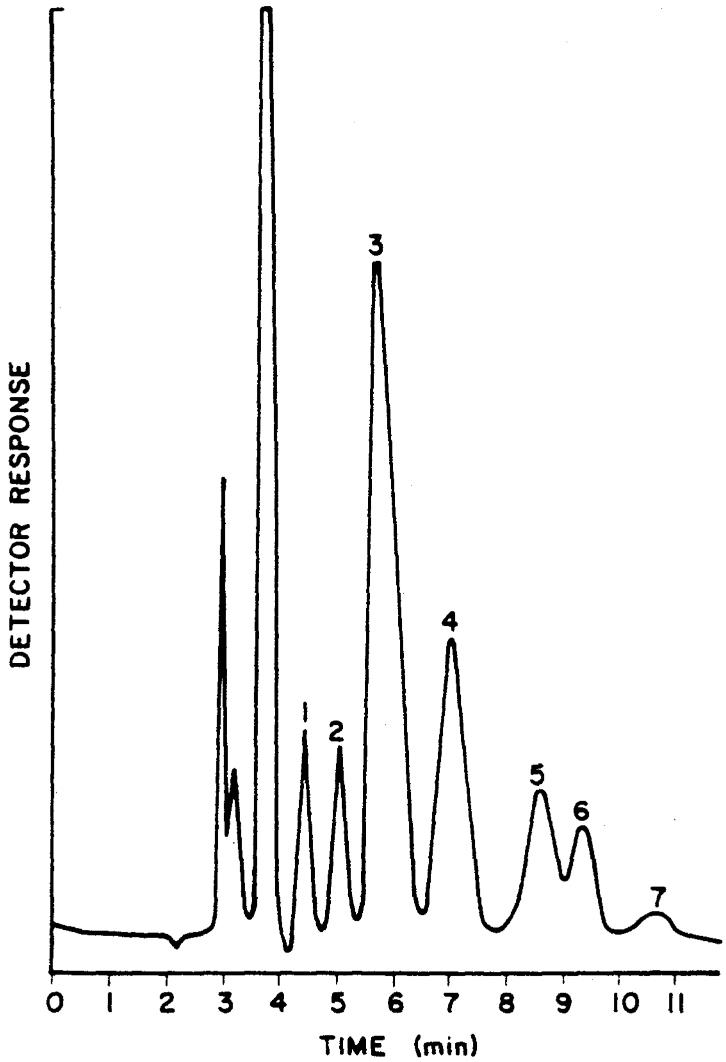

Figure 7: Chromatogram of laboratory saponified coconut oil fatty acids. Identification of acids: (1) caprylic; (2) capric; (3) lauric; (4) myristic; (5) palmitic and linoleic; (6) oleic; (7) stearic. Mobile phase composition: 37/43/25, water/acetonitrile/tetrahydrofuran by volume.

fatty acid composition of tung oil is dominated to the extent of 85% (by weight) (51) by eleostearic acid, 9,11,13-octadecatrionoic acid. Trace constituents, such as linoleic, linolenic, and palmitic acids all elute under the eleostearic peak.

A chromatogram of a laboratory saponified coconut oil using a slightly different solvent mixture than was employed on the previous three chromatograms is shown in Figure 7. The elution

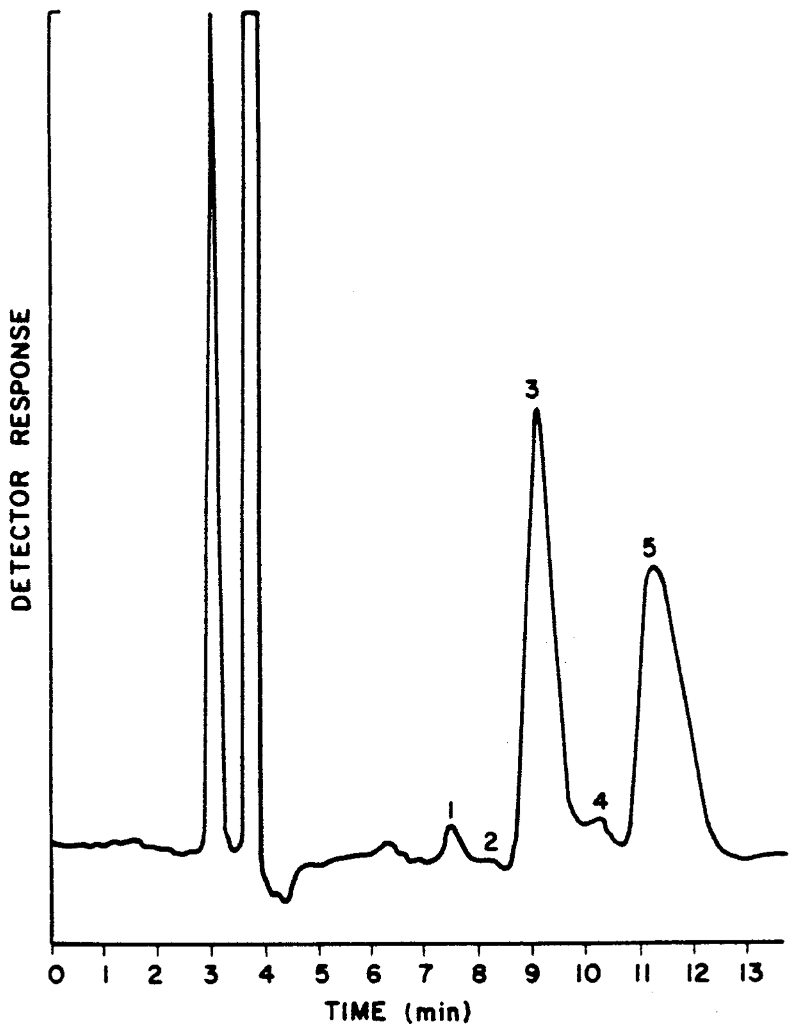

Figure 8: Chromatogram of a commercial stearic acid sample. Identification of acids: (1) myristic; (2) pentadecenoic; (3) palmitic; (4) margaric; (5) stearic. Mobile phase composition same as in Figure 7.

pattern is identical to that exhibited in Figure 4, with the exception that the resolution between particular components is slightly improved by lowering the water content of the ternary eluent and replacing this reduction in water with an equal volume of acetonitrile. In general, we have obtained better resolution for our fatty acid mixtures using a 37/43/25 volume ratio of water/acetonitrile/tetrahydrofuran than by using a 40/40/25 volume ratio. The agreement between laboratory and commercial saponified coconut oil profiles is typical of the results we have obtained

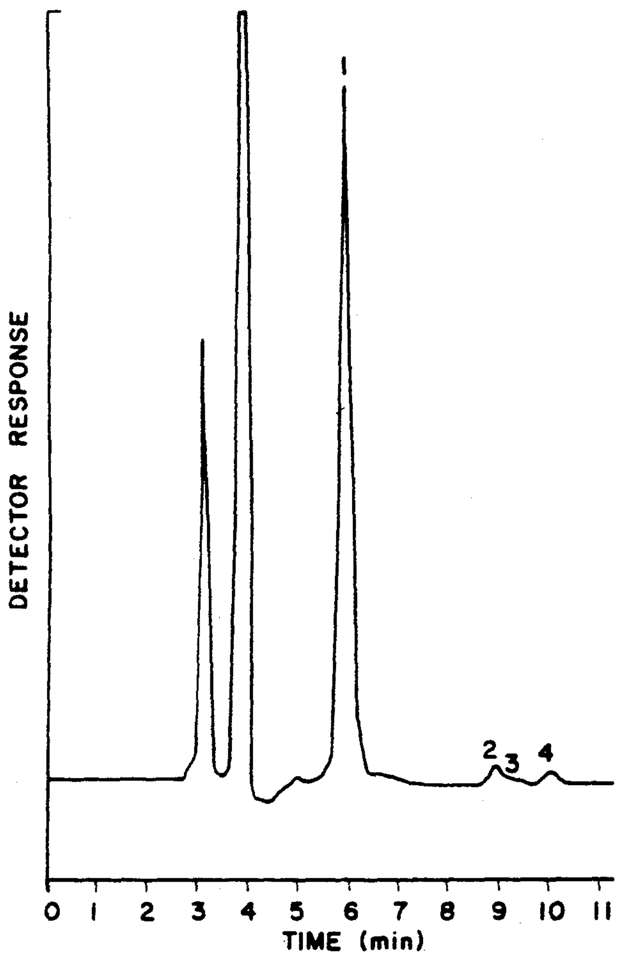

Figure 9: Chromatogram of commercially saponified castor oil fatty acids. Identification of acids: (1) ricinoleic; (2) linoleic; (3) palmitic; (4) oleic. Mobile phase composition same as in Figure 7.

in this study and lends credence to our saponification/extraction technique.

The liquid chromatographic method presented here also has the capability of discerning differences in grades of fatty acids and in monitoring chemical transformations of fatty acids. Figure 8 is the chromatogram of a commercial grade stearic acid sample. In this case, there is considerable palmitic acid in addition to the stearic acid. An additional feature of this chromatogram is the ability to separate and detect odd-carbon number fatty acids, such as pentadecenoic and heptadecenoic acid (margaric acid) from

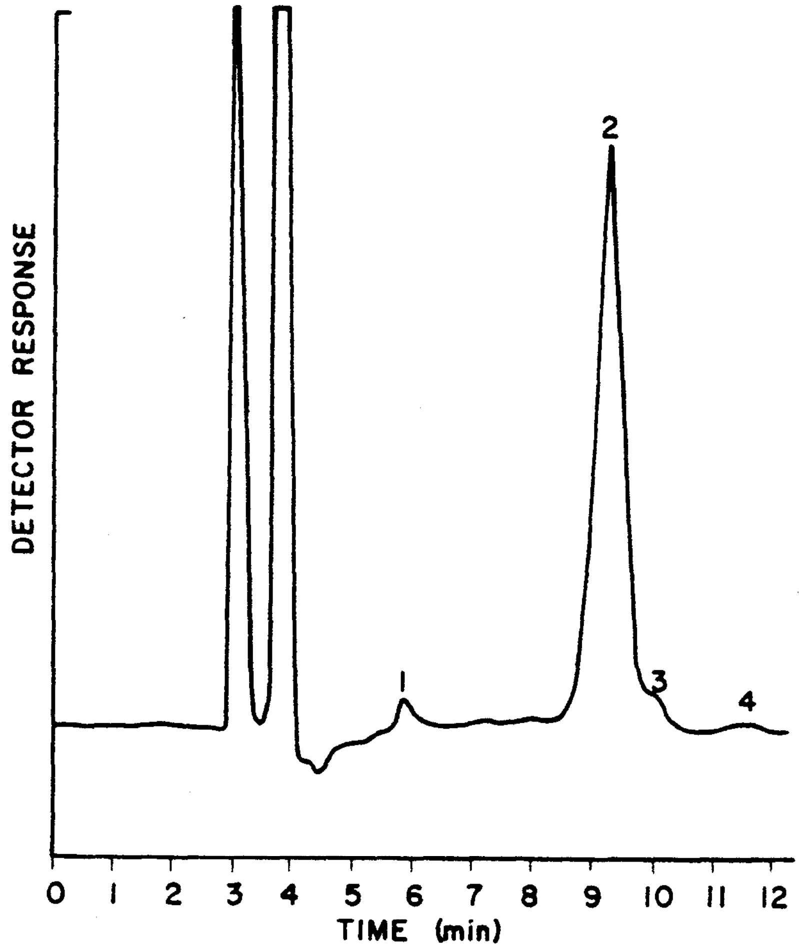

Figure 10. Chromatogram of commercially saponified dehydrated castor oil fatty acids. Identification of acids: (1) ricinoleic; (2) 9,11-octadecadienoic and 9,12-octadecadienoic; (3) oleic; (4) stearic. Mobile phase composition: 37/43/25/2, water/acetonitrile/tetrahydrofuran/acetic acid by volume.

the even-carbon number acids. The latter compound is frequently used as an internal standard in the gas chromatography of fatty acid methyl esters since it does not occur to any appreciable extent in natural oil compositions. It would appear from the results of this chromatogram that it could also serve as an internal standard in our high pressure liquid chromatographic assay.

One particular fatty acid transformation which can be readily followed using our method is the conversion of castor oil fatty acids to dehydrated castor oil fatty acids. This reaction involves the dehydration of ricinoleic acid (12-hydroxy-cis-9-octadecenoic to a mixture of 9,11 and 9,12-octadecadienoic acids. Production of the latter acids confers "drying properties" on alkyd resins containing those acids incorporated in the polymer chain via esterification. The conversion of castor oil by this process is of major importance to the coatings industry. Figure 9 is the chromatogram of commercially saponified castor oil fatty acids. The ricinoleic acid elutes early due to the presence of the hydroxyl group in its structure. This retention trend is typical of fatty acids containing polar functional groups (i.e., hydroxyl, oxirane) other than the carboxyl moiety. Ricinoleic acid represents 90% of the fatty acid composition of castor oil; however, other minor acids are apparent in the chromatogram.

Comparison of Figures 9 and 10 shows a typical conversion of commercially saponified ricinoleic acid to the mixture of conjugated and unconjugated octadecadienoic acids by dehydration. A small quantity of unconverted ricinoleic acid is apparent as well as oleic and stearic acids. The broad peak contains both positional isomers, 9,11-octadecadienoic and 9,12-octadecadienoic acid.

Alkyd Resin Results. We have experienced no difficulty in applying the above liquid chromatographic procedure to alkyd resins. Since these resins are derived from polyesterification reactions between selected acids, polyols, and fatty acids derived from natural oils, the elution characteristics of several alkyd resin constituents were determined on the Free Fatty Acid column. These multifunctional alcohols and acids are tabulated in Table III. All of these highly polar compounds eluted with the solvent front, co-eluting under the vacancy peaks. This confirms their absence in the fatty acid profile should they have been extracted simultaneously with the fatty acids in the n-hexane extraction step.

Figure 11 is the chromatogram of fatty acids derived from a "pure" alkyd resin containing only soya oil, glycerine, and

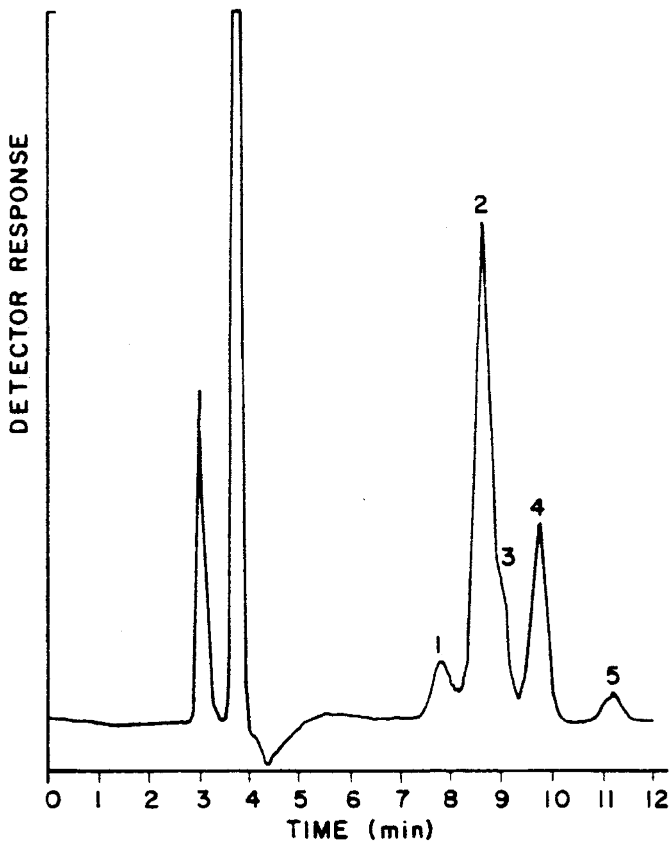

Figure 11. Chromatogram of laboratory saponified soya-based alkyd resin fatty acids. Identification of acids: (1) linolenic; (2) linoleic; (3) palmitic; (4) oleic; (5) stearic. Mobile phase composition same as in Figure 10.

phthalic anhydride. The profile of peaks compares very favorably with the results in Figure 3, using the same solvent system, and confirms that this is a soybean oil based alkyd resin.

A "non-drying" alkyd fatty acid chromatogram is given in Figure 12. The general profile compares well with a coconut oil based alkyd (see Figure 7), with the exception of the ratio of peaks 5 and 6, which are linoleic and palmitic acid, respectively. This is due to the small charge of cottonseed oil (3% by weight of total alkyd ingredients) added along with the coconut oil (27% by weight of total alkyd) in this alkyd synthesis. The high linoleic acid content of cottonseed oil combined with the acidi-

TABLE III

ALKYD CONSTITUENTS NOT RETAINED ON THE FREE FATTY ACID COLUMN

Acids
Fumaric Acid
Maleic Anhydride
Isophthalic Acid
Phthalic Anhydride
Benzoic Acid
Succinic Acid
Terephthalic Acid
Alcohols
Pentaerythritol
Ethylene Glycol
Diethylene Glycol
Mannitol
Glycerol
Propylene Glycol
Trimethylolpropane

fied mobile phase splits the combined palmitic/linoleic acid peak into a pair of peaks.

Figures 13 and 14 were chromatograms of unknown alkyd resin samples submitted for analysis. The chromatographic profile and peak heights strongly suggested a tall oil-based alkyd for both samples. This is based on the ratio of the two predominant acids in the chromatogram, linoleic and oleic acid. In actuality, both resins are tall oil alkyds, containing weight percents of tall oil of 32 and 35%, respectively.

The chromatograms in Figures 13 and 14 differ substantially from other published chromatographic data for tall oils on the Free Fatty Acid column (37). Our peak area ratios correctly correspond to reported values for tall oils (43), however, there are many grades of tall oil. It is obvious that the Free Fatty

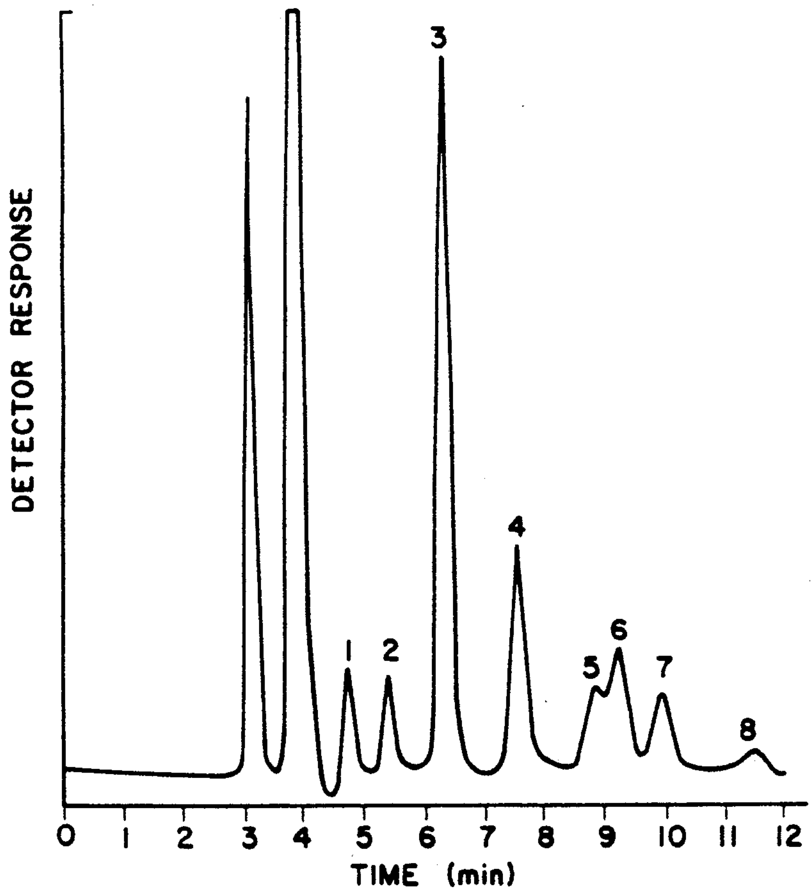

Figure 12: Chromatogram of laboratory saponified non-drying alkyd resin fatty acids. Identification of acids: (1) caprylic; (2) capric; (3) lauric; (4) myristic; (5) linoleic; (6) palmitic; (7) oleic; (8) stearic. Mobile phase composition same as in Figure 10.

Acid column is capable of producing chromatograms which show these differences.

The last two fatty acid chromatograms, derived from alkyd resin saponification, are Figures 15 and 16, and represent profiles derived from a styrenated-acrylated alkyd and rosin-maleic ester modified alkyd, respectively. These alkyd resins have been modified by the addition of vinyl monomers or a maleic anhydride adduct to the polyester backbone (52). The important component in the original alkyd composition is the dehydrated castor oil content which for both resins is approximately 32 weight percent of the initial reactor charge. However, there is a significant

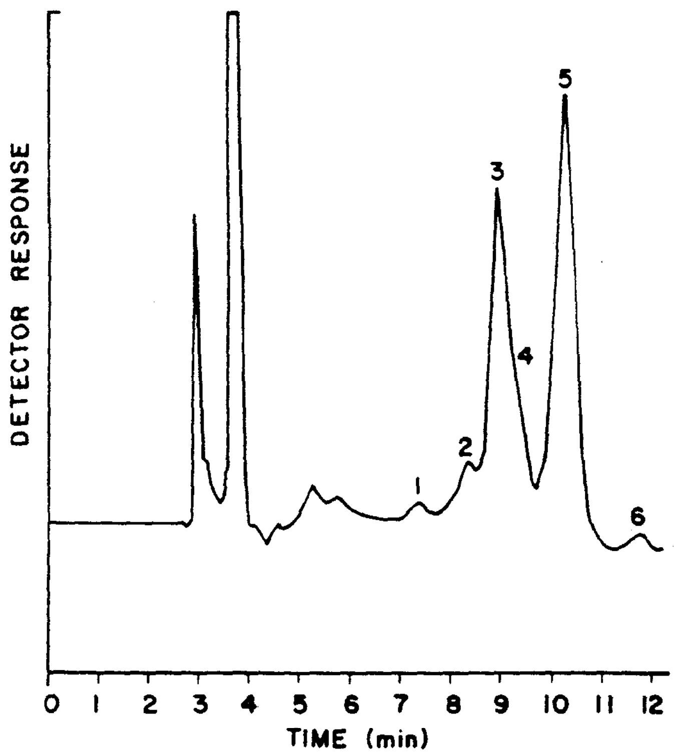

Figure 13: Chromatogram of laboratory saponified tall oil-based alkyd resin fatty acids. Identification of acids: (1) unidentified; (2) palmitoleic or linolenic; (3) linoleic; (4) palmitic; (5) oleic; (6) stearic. Mobile phase composition same as in Figure 10.

difference in how these dehydrated castor oil fatty acids were derived.

The fatty acid composition in Figure 15 represents the final composition in the alkyd resin from a reaction in which dehydrated castor oil was charged to the reactor initially. Note that there is a large amount of unconverted ricinoleic acid in the chromatogram which would suggest that the supplier of this oil had not extensively dehydrated the castor oil. This lot of dehydrated castor oil could have been rejected for synthetic purposes had a liquid chromatographic analysis been run on the initial dehydrated castor oil.

In Figure 16, the dehydrated castor oil fatty acids have been produced in-situ during the alkyd synthesis. The resultant fatty acid composition is quite different from the chromatographic pro-

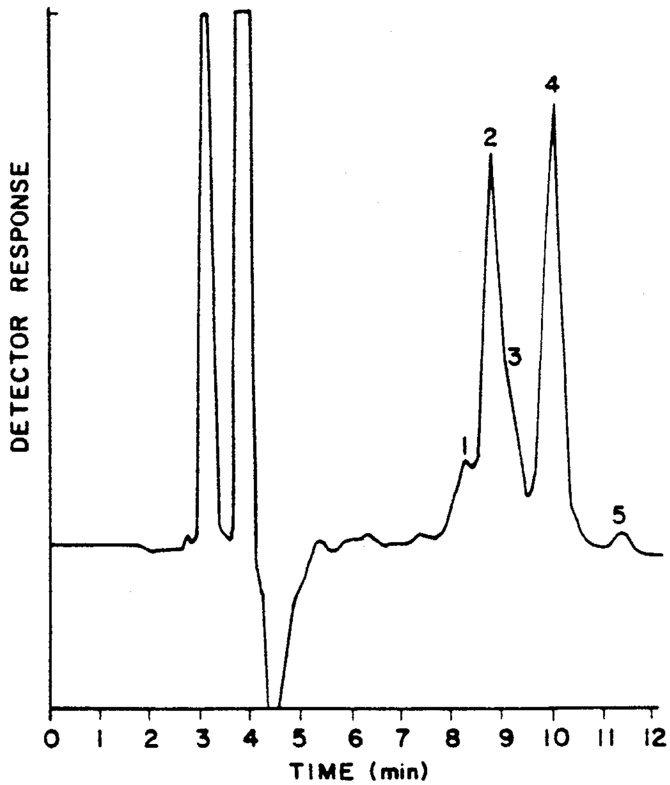

Figure 14: Chromatogram of laboratory saponified tall oil-based alkyd resin fatty acids. Identification of acids: (1) palmitoleic or linolenic; (2) linoleic; (3) palmitic; (4) oleic; (5) stearic. Mobile phase composition same as in Figure 10.

file in Figure 15. There is a large quantity of unconverted ricinoleic acid and a number of fatty acids which are normally not associated with dehydrated castor oil and/or castor oil (see Figures 9 and 10). One of the acids, undecylenic acid, is produced commercially by pyrolytic decomposition of castor oil. This would seem to infer that the high temperatures in the reactor contribute to the decomposition of castor oil. Hence, the resultant polymer will be quite different from that produced in a synthesis based on totally converted castor oil.

Quantitative Aspects. Excellent quantitative results have been obtained in our laboratory using the Free Fatty Acid column/mobile phase combinations mentioned above. Chromatographic analysis of

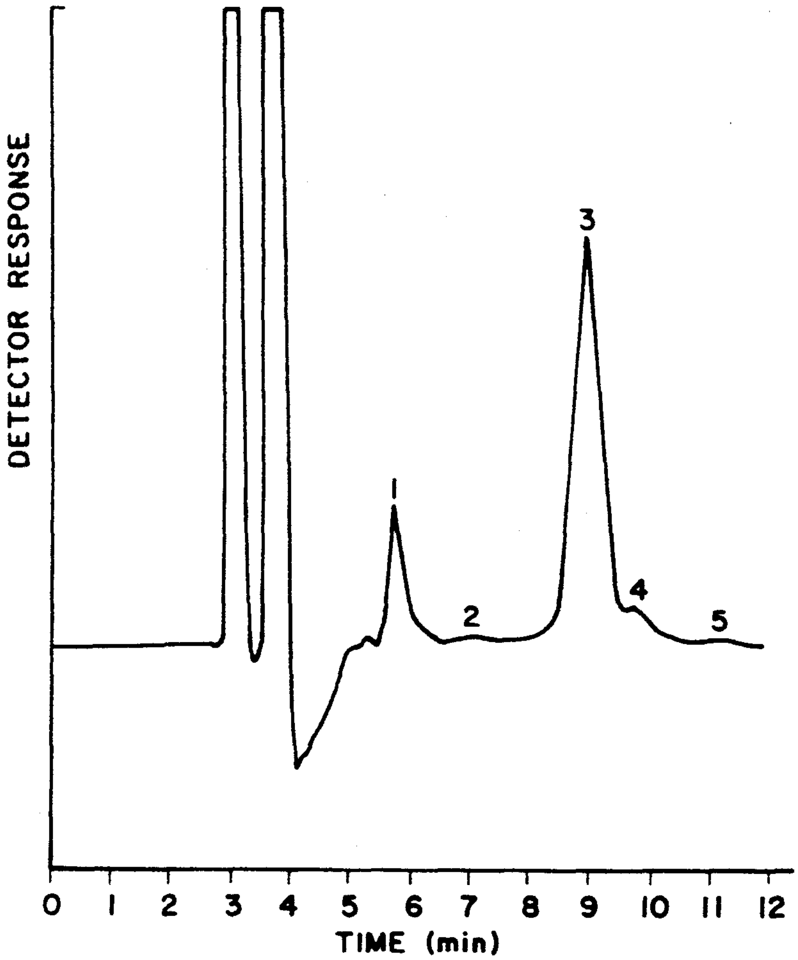

Figure 15: Chromatogram of laboratory saponified styrenated-acrylated alkyd resin fatty acids. Identification of acids: (1) ricinoleic; (2) myristic; (3) 9,11-octadecadienoic and 9,12-octadecadienoic; (4) oleic; (5) stearic. Mobile phase composition same as in Figure 10.

coconut, soya, and castor oil derived fatty acid mixtures have yielded agreement for individual component fatty acids within 1-3% of compositions determined by methyl ester gas-liquid chromatographic analysis. These results have been obtained on liquid chromatographic peaks which were uncorrected for detector response. It should be noted that comparisons to reported compositions of commercial oils are not entirely significant, since composition of certain major components in fatty acid mixtures derived from natural oil sources may vary as much as 5%. The

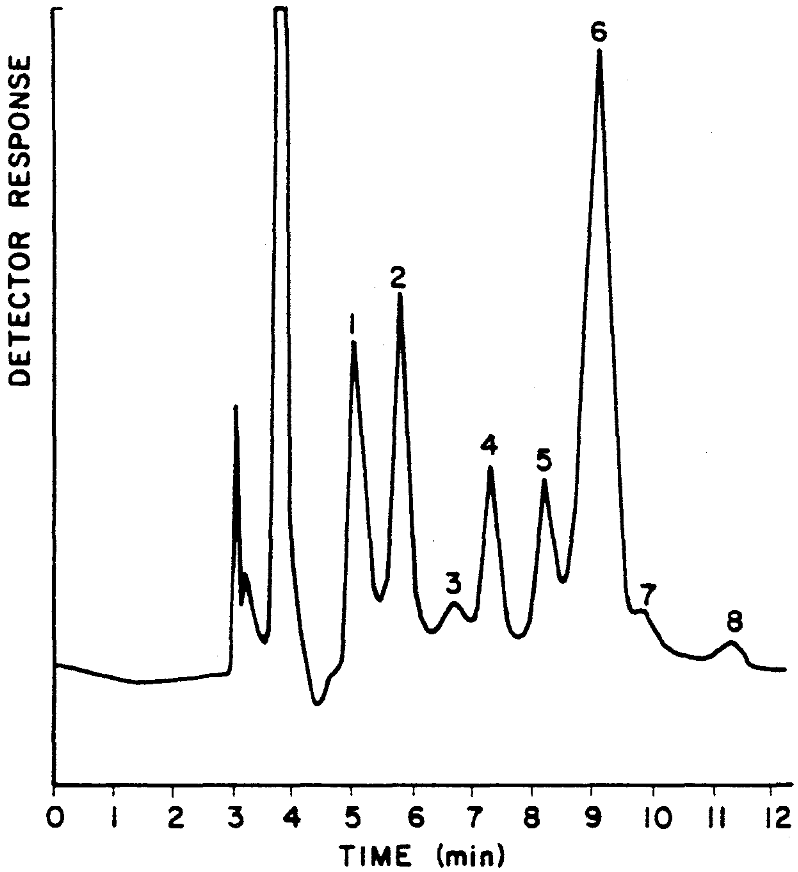

Figure 16: Chromatogram of laboratory saponified rosin-maleic ester modified alkyd fatty acids. Identification of acids: (1) undecylenic; (2) ricinoleic; (3) cis or trans-9-hexadecenoic; (4) myristic; (5) linolenic; (6) 9,11-octadecadienoic and 9,12-octadecadienoic; (7) oleic; (8) stearic. Mobile phase composition same as in Figure 10.

variation is a result of the varied environments under which such natural oils are derived.

For example, in Table IV uncorrected peak areas have been normalized for the stearic acid mixture in Figure 8. When this data is compared to results obtained from GC analysis (53,54), one can see that typical stearic acid mixtures varied over an eight-year period. In this context, the comparison of the liquid and gas chromatographic results is quite good.

Table V affords an actual comparison between liquid and gas chromatographic results obtained on the same fatty acid mixture.

TABLE IV

FATTY ACID COMPOSITION OF COMMERCIAL STEARIC ACID SAMPLE

	HPLC (1976)	GLC (1966)	GLC (1974)
Fatty Acid	% Total	% Total	% Total
Myristic	1.6	2.5	2.5
Pentadecenoic	0.1	0.5	0.5
Palmitic	48.7	53.0	50.0
Margaric	3.7	2.0	1.5
Stearic	45.9	42.0	45.5

TABLE V

COMPARISON OF FATTY ACID COMPOSITIONS DETERMINED BY HPLC AND GC

	HPLC	GC
Fatty Acid	% Total	% Total
Caprylic	1.2	0.3
Capric	2.0	1.4
Lauric	58.3	56.0
Myristic	21.3	23.4
Palmitic	7.9	9.5
Linoleic	0.8	0.3
Stearic	1.6	1.9
Oleic	7.1	7.3

The gas chromatograph results were corrected for detector response while the liquid chromatographic data was obtained by normalizing peak heights uncorrected for refractometer response. In general, the agreement is moderately good and would undoubtedly be better if the liquid chromatographic peaks were corrected for detector response. It should be noted that the HPLC analysis took 4-1/2 minutes per sample.

TABLE VI

COMPARISON OF FATTY ACID COMPOSITION OF COCONUT OIL ANALYZED OVER A THREE-WEEK PERIOD BY HPLC

Fatty Acid	1st Week % Total	2nd Week % Total	3rd Week % Total
Caprylic	2.2	2.1	2.1
Capric	3.2	3.1	3.4
Lauric	46.1	45.7	45.8
Myristic	20.0	19.8	19.8
Palmitic + Linoleic	15.1	15.2	14.9
Oleic	8.9	9.2	9.2
Stearic	3.8	4.4	4.1
Unidentified Peaks	0.7	0.5	0.7

The stability of this analytical method is indicated by the results presented in Table VI. The compositional data reported for a coconut oil fatty mixture was taken over a three-week time span. Each assay was taken approximately one week apart on the same sample. The agreement for the percentages of fatty acid is usually within 0.1-0.2%, quite acceptable for fatty acid analysis.

In summary, the above column/mobile phase system is capable of rapidly determining the fatty acid composition of commercial oils and alkyd resins. With appropriate adjustment of the mobile phase, quantitation of many of the component fatty acids can be made possible. The results of studies on marine oils, incorporating ultraviolet as well as refractive index detection, will be presented in the near future as well as the analysis of fatty alcohols.

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